Stereoselective epoxidation of vinyl sulfones and *N*-(*p*-tolylsulfonyl)-vinylsulfoximines derived from isopropylideneglyceraldehyde: synthesis of chiral building blocks

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Epoxidation of *N*-(*p*-tolylsulfonyl)vinylsulfoximines using metal alkyl peroxides proceeds with varying degrees of stereoselectivity, depending both on the metal cation and the steric bulk of the alkyl peroxide group. The stereochemical outcome of the epoxidation of substrates bearing an allylic asymmetric centre is also dependent upon the epoxidising agent, and very high levels of stereoselectivity may be obtained in the formation of sulfonyloxirane **8a**. This oxirane was subsequently converted into the sulfonyloxirane **15**, a precursor to a useful chiral functionalised acyl anion equivalent. In addition, the optically pure α-bromothioester **20** was also prepared.

We have been interested for some time in the stereoselective preparation of heterosubstituted oxiranes using the nucleophilic epoxidation of electron-deficient alkenes. Diastereoselective epoxidation of 1-(*p*-tolylthio)-1-nitroalkenes derived from enantiomerically pure α-hydroxy- and α-amino-aldehydes, followed by stereospecific ring-opening of the product epoxides, has allowed the stereoselective preparation of derivatives of β-hydroxy-α-amino acids[1] and α-hydroxy-β-amino acids,[2] respectively. We have also been interested in the epoxidation of vinyl sulfones with allylic stereocentres, and have investigated how the sense of diastereoselectivity is dependent upon the nature of the epoxidising reagent and the substrate.[3,4] In order to avoid the need for an existing stereogenic centre within the carbon backbone, we have investigated the low-temperature epoxidation of *N*-(*p*-tolylsulfonyl)vinylsulfoximines using lithium *tert*-butyl peroxide which gave *N*-(*p*-tolylsulfonyl)sulfoximinooxiranes with high diastereoselectivity.[5] This process has recently been extended to the corresponding vinyl sulfoxides by the use of sodium *tert*-butyl peroxide as the oxidant.[6,7]

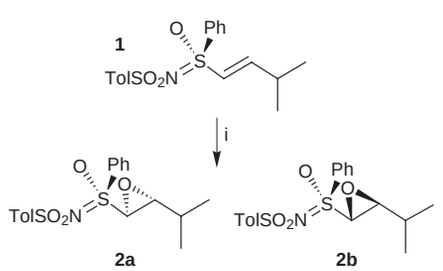
These results raise the question as to how the overall stereochemical outcome of a nucleophilic epoxidation of a substrate containing both a stereogenic centre within the carbon backbone and a stereogenic centre within the electron-withdrawing group might be controlled. Can an appropriate choice lead to very high levels of stereochemical control? We have therefore addressed this question by investigating the stereochemical outcome of the nucleophilic epoxidation of a series of vinyl sulfones and vinylsulfoximines derived from (*R*)-isopropylideneglyceraldehyde. The products of these reactions have then been converted into useful chiral building blocks to illustrate the potential value of the process.†

Since one of the principal methods for controlling the stereochemical outcome of nucleophilic epoxidation reactions involves changing the nature of the epoxidising agent, we have further investigated the nucleophilic epoxidation of *N*-(*p*-tolylsulfonyl)vinylsulfoximines using potassium *tert*-butyl peroxide,[9] as well as the bulkier reagents, lithium and potassium triphenylmethyl peroxide.‡

† The majority of the work described in this manuscript has been described in a preliminary communication (see ref. 8).
‡ The base catalysed epoxidation of an enone using triphenylmethyl hydroperoxide has been reported (see ref. 10).

Results and discussion

Epoxidation of the racemic vinylsulfoximine **1** with potassium *tert*-butyl peroxide in tetrahydrofuran (THF) proceeded very rapidly at −78 °C to give a mixture of the two stereoisomeric oxiranes **2a** and **2b** (ratio 10:11). This result is in sharp contrast to the results obtained using lithium *tert*-butyl peroxide, in which oxirane **2a** was formed with high stereoselectivity (the sense of which was established by X-ray crystallography).[5] The fact that such a markedly different result was obtained under reaction conditions which were closely comparable, provides very strong support for the suggestion[5] that there is an interaction between the lithium cation and the sulfoximine group during lithium *tert*-butyl peroxide epoxidations. Epoxidation with lithium triphenylmethyl peroxide proceeded with very high diastereoselectivity to give **2a**, whilst epoxidation with potassium triphenylmethyl peroxide gave **2a** and **2b** with moderate selectivity in favour of **2a** (4:1) (Scheme 1). Our results are summarised in Table 1.



Scheme 1 *Reagents and conditions:* i, MOOR, THF, −78 °C (see Table 1 for reagents).

Having established that the stereoselectivity was dependent upon the choice of epoxidising agent, we set out to investigate the epoxidation of substrates possessing an additional stereogenic centre. As initial substrates, we chose the vinyl sulfone **3** derived from (*R*)-isopropylideneglyceraldehyde, together with the two diastereoisomeric *N*-(*p*-tolylsulfonyl)vinylsulfoximines **4** and **5** derived from (*S*)-(+)- and (*R*)-(−)-*S*-methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximines, **6** and **7** respectively. The vinyl sulfone **3** was prepared using the general method reported by Lee and Oh,[11] and the vinylsulfoximines **4** and **5** were prepared using our previously reported general procedure.[5]

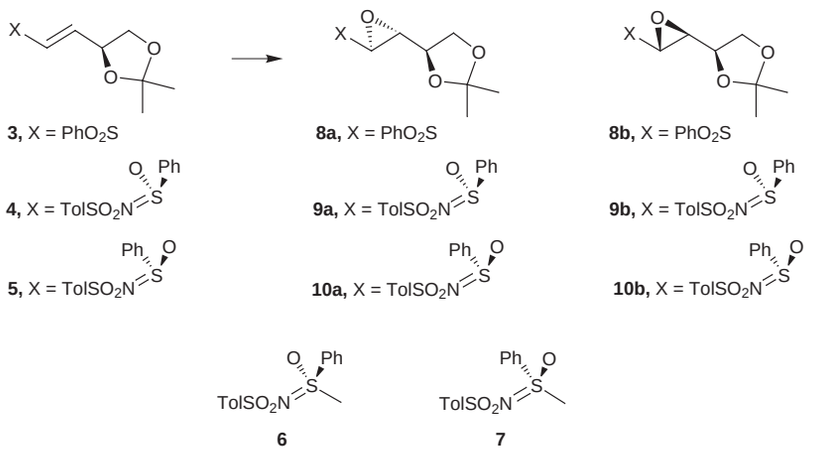


Table 1 Epoxidation of vinylsulfoximine **1**

Reagent	Ratio **2a**:**2b**[a]	Yield (%)[b]
LiOO^{t}Bu	25:1	97
$LiOOCPh_3$	25:1	73
KOO^{t}Bu	10:11	76
$KOOCPh_3$	4:1	74

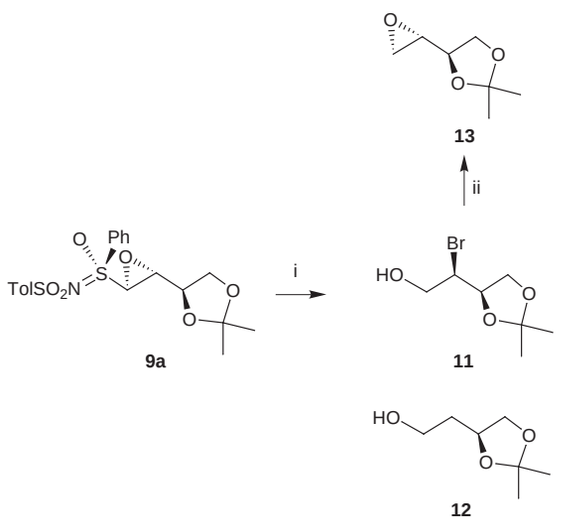
[a] Diastereoisomer ratios were determined from ^{1}H NMR spectra of crude reaction mixtures; a ratio of 25:1 implies that the minor isomer could not be detected. [b] Yields are of purified material.

Epoxidation of the vinyl sulfone **3** with each of the four epoxidising agents under our standard conditions at −20 °C in THF gave a mixture of the *anti* oxirane **8a** and the *syn* oxirane **8b**, with varying selectivity in favour of the *anti* compound (Table 2). Of special note was the excellent diastereoselectivity in favour of **8a** obtained using potassium triphenylmethyl peroxide, which allows easy access to a potentially useful chiral building block (*vide infra*). The results for the epoxidation of the vinylsulfoximines **4** and **5** at −78 to −55 °C are also indicated in Table 2. The results obtained using both lithium *tert*-butyl peroxide and lithium triphenylmethyl peroxide are complex, and not easily rationalised. Clearly there are several possible sites for lithium coordination in **4** and **5**, and the combination of stereogenic centres in **5** combines to make epoxidation with lithium *tert*-butyl peroxide poorly stereoselective, whilst the reaction with lithium triphenylmethyl peroxide seems completely independent of the sulfoximine stereochemistry. In contrast, epoxidation of all three substrates with potassium *tert*-butyl peroxide demonstrates clear reinforcing stereoinduction for **5** and non-reinforcing stereoinduction for **4**.

The *anti* stereochemistry of **9a** was established directly by X-ray crystal structure analysis.[8] Further corroboration of this result was obtained by conversion of the sulfoximinooxirane **9a** into the corresponding bromohydrin **11** (68%) by our method involving ring-opening with magnesium bromide–diethyl ether (to give the α-bromoaldehyde) in the presence of tetra-*n*-butylammonium borohydride as *in situ* reducing agent.[12] Protected butane-1,2,4-triol **12** was obtained (21%) as a by-product in this process. Treatment of **11** with sodium hydride in diethyl ether gave the known oxirane **13** (Scheme 2), which was identified by comparison of ^{1}H NMR data with those in the literature.[13] Other routes to oxirane **13** have been described.[14–16]

This result confirms unambiguously that the conversion of **9a** into **11** occurs with inversion of configuration at C-2. Analogous treatment of the 6:1 mixture of oxiranes **10a** and **10b**, obtained by potassium *tert*-butyl peroxide epoxidation of **5**, gave a mixture of **11** and its C-2 epimer (in a ratio of 6:1), thereby establishing that the major isomer had the same configuration at C-2 as **9a**, and therefore had structure **10a**.

The stereochemistry of the *anti* sulfonyloxirane **8a** was established by a single crystal X-ray crystallographic determination



Scheme 2 *Reagents and conditions:* i, $MgBr_2$, Bu_4NBH_4, Et_2O–CH_2Cl_2, 24 h, room temp.; ii, NaH, Et_2O, room temp.

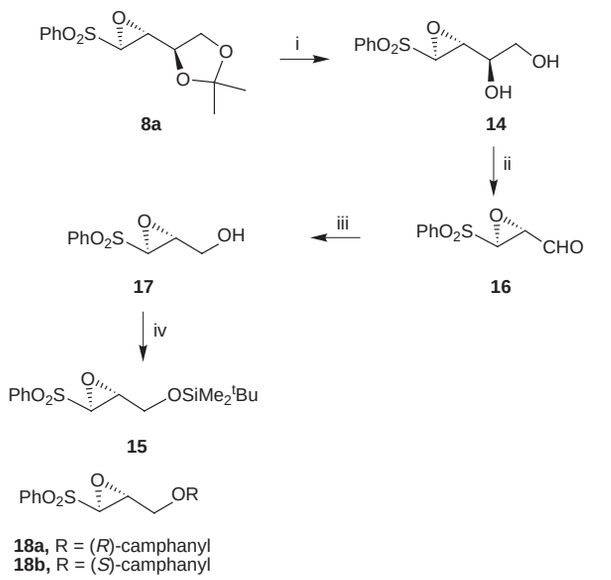
of the diol **14**,[8] obtained by cleavage of the isopropylidene acetal (*vide infra*). Following our preliminary communication, a closely related stereoslective epoxidation of the corresponding (*Z*)-vinyl sulfone was reported.[17] To illustrate one potential synthetic application of the sulfonyloxirane **8a**, we have established a method for its conversion into (2*S*,3*R*)-2-phenylsulfonyl-3-*tert*-butyldimethylsilyloxymethyloxirane **15**. We have previously established that the lithio-derivative of this compound, in racemic form, is a versatile functionalised acyl anion equivalent,[18] and may be used for the preparation of unsubstituted epoxyketones,[19] for example. Thus, treatment of the diol **14** with sodium metaperiodate gave the aldehyde **16**, which was reduced with sodium borohydride to the alcohol **17** (Scheme 3). The enantiomeric purity of the alcohol **17** was established by conversion into the (*R*)- and (*S*)-camphanate esters§ **18a** and **18b**, which were shown to be diastereoisomerically pure within the limits of detection by ^{1}H NMR. Finally, protection of the alcohol **17** as the *tert*-butyldimethylsilyl ether gave the target **15**, identical by comparison of spectroscopic data with the racemic compound.[18]

As further proof of the stereochemical course of these epoxidation reactions, the α-thiophenyl sulfonyloxirane **19** [prepared by treatment of **8a** with *n*-BuLi and phenyl benzenethiosulfonate ($PhSSO_2Ph$)] was treated with $MgBr_2$ to afford the corresponding *syn* α-bromo thioester **20** (Scheme 4). The structure of this compound was determined by comparison of its ^{1}H NMR spectra with the corresponding spectra of both diastereo-

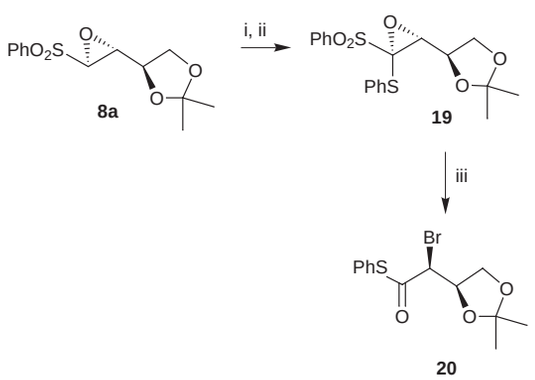
§ The IUPAC name for camphanoic acid is hexahydro-3a,4-dimethyl-1-oxocyclopenta[*c*]furan-4-carboxylic acid.

Table 2 Epoxidation of vinyl sulfone **3**, and vinylsulfoximines **4** and **5**

	Alkene	Oxirane	^{t}BuOOLi	Ph_3COOLi	^{t}BuOOK	Ph_3COOK
	3	**8a/8b**	4:3 (85%)	5:4 (78%)	4:1 (68%)	25:1 (76%)
	4	**9a/9b**	25:1 (68%)	25:1 (65%)	2:1 (80%)	25:1 (67%)
	5	**10a/10b**	2:1 (75%)	25:1 (76%)	6:1 (80%)	7:4 (74%)



Scheme 3 *Reagents and conditions:* i, *p*-TSA, THF–MeOH, 24 h, room temp.; ii, $NaIO_4$, MeOH, H_2O, −25 °C; iii, $NaBH_4$, MeOH, −25 °C; iv, ^{t}BuMe$_2$SiCl, imidazole, DMF, room temp.



Scheme 4 *Reagents and conditions:* i, BuLi, THF, −102 °C; ii, $PhSSO_2$-Ph; iii, $MgBr_2$, Et_2O, room temp.

isomers of the related α-bromo *p*-tolylthioester,[1] whose structures had already been unambiguously established by X-ray crystallography.[20]

Experimental

General experimental procedures and instrumentation are as previously described.[18] *J* values are given in Hz. $[a]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. Light petroleum refers to that fraction with boiling point range 40–60 °C. All organic extracts were dried over anhydrous $MgSO_4$, and solvent was removed using a rotary evaporator.

(*S*)-(*E*)-2,2-Dimethyl-4-[2-(phenylsulfonyl)ethenyl]-1,3-dioxolane 3

n-Butyllithium (5.6 ml, 2.5 M in hexanes, 14.1 mmol) was added dropwise to a solution of methyl phenyl sulfone (1.00 g, 6.4 mmol) in dry THF (40 ml) at 0 °C, and the resulting yellow suspension was stirred at 0 °C for 30 min. Diethyl chlorophosphate (1.33 g, 1.11 ml, 7.68 mmol) was added dropwise at that temp., and the yellow solution stirred at 0 °C for a further 30 min. The reaction mixture was cooled to −78 °C and (+)-2,3-*O*-isopropylidene-D-glyceraldehyde[21,22] (1.0 g, 7.68 mmol) was added. The resulting solution was stirred at −78 °C until all the starting material had reacted as judged by TLC analysis. The solution was quenched using aqueous NH_4Cl (saturated, 70 ml) and was allowed to warm to room temp. The aqueous phase was extracted with ethyl acetate (2 × 70 ml), and the organic phase dried and concentrated under reduced pressure. Purification of the residue by flash chromatography using hexane–ethyl acetate (starting with 10:1, then 5:1) gave the vinyl sulfone **3** (1.286 g, 4.8 mmol, 75%) as a colourless crystalline solid, mp 29–30 °C, $[a]_D^{20}$ +8.9 (*c*, 0.9 CH_2Cl_2). Spectroscopic data were identical with those previously reported.[23]

(*S**)-*S*-[(4*S**)(*E*)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethenyl]-*N*-[(4-methylphenyl)sulfonyl]-*S*-phenylsulfoximine 4

(*S*)-*S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine **6** (3.09 g, 10 mmol) was condensed with (+)-2,3-*O*-isopropylidene-D-glyceraldehyde using the method described in our previous publication,[5] to give the pure vinylsulfoximine **4** as a colourless oil (2.655 g, 6.3 mmol, 63%), $[a]_D^{20}$ +18.2 (*c*, 2.0 CH_2Cl_2); δ_H (200 MHz, $CDCl_3$) 1.36 (3H, s, Me_AMe_BC), 1.37 (3H, s, Me_AMe_BC), 2.40 (3H, s, $MeC_6H_4SO_2$), 3.71 (1H, dd, ^2J 8.5 and ^3J 6.5, CH_AH_BCH), 4.18 (1H, dd, ^2J 8.5 and ^3J 7.0, CH_AH_BCH), 4.72 (1H, m, CH_AH_BCH), 6.70 (1H, dd, ^3J 15.0 and 1.5, CH=CHS), 6.99 (1H, dd, ^3J 15.0 and 5.0, CH=CHS), 7.23–7.27 (2H, m, Ar), 7.52–7.71 (3H, m, Ar), 7.81–7.98 (4H, m, Ar).

(*R**)-*S*-[(4*S**)(*E*)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)ethenyl]-*N*-[(4-methylphenyl)sulfonyl]-*S*-phenylsulfoximine 5

(*R*)-*S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine **7** (3.09 g, 10 mmol) was condensed with (+)-2,3-*O*-isopropylidene-D-glyceraldehyde using the method described in our previous publication,[5] to give the pure vinylsulfoximine **5** as a colourless oil (2.74 g, 6.5 mmol, 65%),[5] $[a]_D^{20}$ +1.5 (*c*, 1.0 CH_2Cl_2); δ_H (200 MHz, $CDCl_3$) 1.34 (3H, s, Me_AMe_BC), 1.40 (3H, s, Me_AMe_BC), 2.36 (3H, s, $MeC_6H_4SO_2$), 3.68 (1H, dd, ^2J 8.5 and ^3J 7.0, CH_AH_BCH), 4.18 (1H, dd, ^2J 8.5 and ^3J 7.0, CH_AH_BCH), 4.69 (1H, m, CH_AH_BCH), 6.70 (1H, dd, ^3J 14.5 and 1.5, CH=CHS), 6.99 (1H, dd, ^3J 14.5 and 3.5, CH=CHS), 7.19–7.26 (2H, m, Ar), 7.48–7.67 (3H, m, Ar), 7.78–7.96 (4H, m, Ar).

Epoxidation of vinyl sulfone 3 with lithium/potassium *tert*-butyl/triphenylmethyl peroxide. General procedures

Lithium *tert*-butyl/triphenylmethyl peroxide. To the alkyl hydroperoxide (3.3 equiv.) in dry THF (1 ml per 0.1 mmol) at −78 °C, *n*-butyllithium (solution in hexanes; 2.5 equiv.) was added, dropwise, and allowed to stir for 5 min at that temperature. After 5 min, the vinyl sulfone in dry THF (1 ml per 0.1 mmol) was added, dropwise, and allowed to warm to −20 °C over 10 min. The reaction mixture was stirred for a further 2 h. After 2 h, the reaction was quenched with aqueous NH_4Cl (10%; 1 ml per 0.2 mmol) and Na_2SO_3 (10%; 1 ml per 0.4 mmol), and allowed to warm to room temp. The layers were separated and the product was extracted with CH_2Cl_2 (3 × 1 ml per 0.2 mmol). The combined extracts were dried, concentrated under reduced pressure and purified by column

chromatography (5:1 petrol–ethyl acetate) to give the phenylsulfonyloxirane as a colourless solid (or oil).

Potassium *tert*-butyl/triphenylmethyl peroxide. To potassium hydride in dry THF (1 ml per 0.2 mmol) at −78 °C, the alkyl hydroperoxide (3.3 equiv.) (1 ml per 0.2 mmol) in dry THF was added, dropwise, and allowed to stir for 5 min at that temperature. After 5 min, the vinyl sulfone in dry THF (1 ml per 0.1 mmol) was added, dropwise, and allowed to warm to −20 °C over 10 min. The reaction mixture was stirred for a further 2 h. After 2 h, the reaction was quenched with aqueous NH_4Cl (10%; 1 ml per 0.2 mmol) and Na_2SO_3 (10%; 1 ml per 0.4 mmol), and allowed to warm to room temp. The layers were separated and the product was extracted with CH_2Cl_2 (3 × 1 ml per 0.2 mmol). The combined extracts were dried, concentrated under reduced pressure and purified by column chromatography to give the corresponding phenylsulfonyloxirane as a colourless solid (or oil).

(4*R*)-2,2-Dimethyl-4-[2α(*R**),3β(*S**)-3-(phenylsulfonyl)oxiran-2-yl]-1,3-dioxolane 8a

Treatment of (*S*)-(*E*)-2,2-dimethyl-4-[2-(phenylsulfonyl)-ethenyl]-1,3-dioxolane **3** (0.268 g, 1 mmol) with potassium triphenylmethyl peroxide according to the procedure described above, including purification using flash chromatography and eluting with 8:1 toluene–ethyl acetate, gave the *anti*-oxirane **8a** (0.241 g, 0.85 mmol, 85%), as a colourless crystalline solid, mp 43–44 °C, $[\alpha]_D^{20}$ +54 (*c*, 1.0 CH_2Cl_2) (Found: C, 54.8; H, 5.3. $C_{13}H_{16}O_5S$ requires C, 54.9; H, 5.7%); ν_{max}(KBr)/cm^{-1} 3070, 2988, 1380, 1315, 1090, 754; δ_H (200 MHz, $CDCl_3$; standard Me_4Si) 1.34 and 1.44 (6H, 2 × s), 3.75–3.77 (1H, m), 3.84–3.94 (1H, m), 4.11 (3H, m), 7.57–7.76 (3H, m), 7.90–7.97 (2H, m); δ_C (50 MHz, $CDCl_3$) 134.6, 129.4, 128.8, 128.4, 110.6, 72.9, 66.4, 66.0, 57.4, 26.4, 25.1; *m*/*z* (FAB) 285 (MH^+, 60%), 259 (80), 227 (40), 199 (40), 125 (60), 77 (60). The *syn*-oxirane **8b**, which was present as the minor component in the reaction using lithium *tert*-butyl peroxide as the oxidant, exhibited the following ^{13}C NMR data: δ_C 134.6, 129.4, 128.8, 128.4, 110.6, 72.1, 65.8, 63.1, 56.5, 25.9, 25.5. It was not possible to isolate a pure sample of **8b**.

Epoxidation of vinylsulfoximines 4 and 5 with lithium/potassium *tert*-butyl/triphenylmethyl peroxide. General procedures

Lithium *tert*-butyl/triphenylmethyl peroxide. To the alkyl hydroperoxide (1.2 equiv.) in dry THF (1 ml per 0.1 mmol) at −78 °C, *n*-butyllithium (solution in hexanes; 1.5 equiv.) was added, dropwise, and allowed to stir for 5 min at that temperature. After 5 min, the vinylsulfoximine in dry THF (1 ml per 0.1 mmol) was added quickly, such that the temperature of the reaction mixture rose to −55 °C. The reaction mixture was warmed to −35 °C over 3 min and cooled to −78 °C, before being quenched with solid sodium sulfite and stirred for a further 15 min. After 15 min, the reaction mixture was diluted with CH_2Cl_2 and allowed to warm to room temp. and filtered through Celite and concentrated under reduced pressure to give the crude product. Purification by column chromatography (3:1 petrol–ethyl acetate) gave the pure sulfoximinooxirane.

Potassium *tert*-butyl/triphenylmethyl peroxide. To potassium hydride (1.5 equiv.) in dry THF (1 ml per 0.2 mmol) at −78 °C, the alkyl hydroperoxide (1.2 equiv.) (1 ml per 0.2 mmol) in dry THF was added, dropwise, and allowed to stir for 5 min at that temperature. After 5 min, the vinylsulfoximine in dry THF (1 ml per 0.1 mmol) was added, dropwise, and allowed to warm to −35 °C over 5 min. The reaction mixture was re-cooled to −78 °C and quenched with aqueous NH_4Cl (10%; 1 ml per 0.2 mmol) and Na_2SO_3 (10%; 1 ml per 0.4 mmol), and allowed to warm to room temp. The layers were separated and the product was extracted with CH_2Cl_2 (3 × 1 ml per 0.2 mmol). The combined extracts were dried, concentrated under reduced pressure and purified by column chromatography (3:1 petrol–ethyl acetate) to give the corresponding sulfoximinooxirane.

(*R*)-*S*-[(4*R*),2α(*R**),3β(*S**)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)oxiran-2-yl]-*N*-[(4-methylphenyl)sulfonyl]-*S*-phenylsulfoximine 9a

Treatment of the vinylsulfoximine **4** (0.84 g, 2 mmol) with lithium *tert*-butyl peroxide gave the *anti*-oxirane **9a** (0.594 g, 1.36 mmol, 68%) as a colourless crystalline solid, mp 99–101 °C, $[\alpha]_D^{20}$ +86.8 (*c*, 0.6 CH_2Cl_2); ν_{max}(film)/cm^{-1} 1599, 1497, 1325, 1065; δ_H (200 MHz, $CDCl_3$) 1.31 (3H, s, Me_A*Me*$_B$C), 1.35 (3H, s, *Me*$_A$Me$_B$C), 2.40 (3H, s, *Me*$C_6H_4SO_2$), 3.59 (1H, dd, ^3J 4.0 and 1.5, C*H*[O]CHS), 3.85–3.92 (1H, m, C*H*CH_2CMe_2), 4.07–4.17 (2H, m, CHC*H*$_2$CMe_2), 4.57 (1H, d, ^3J 1.5, CH[O]-C*H*S), 7.24–7.28 (2H, m, Ar), 7.58–7.79 (3H, m, Ar), 7.82–8.01 (4H, m, Ar); *m*/*z* (EI) 422 (M^+ − Me, 4.8), 278 (PhSNTs, 20%) (Found: M^+ − Me, 422.0715. $C_{19}H_{20}NO_6S_2$ requires 422.0732). The *syn*-oxirane **9b**, which was obtained by column chromatography from the reaction using potassium *tert*-butyl peroxide as the oxidant, was a colourless oil: $[\alpha]_D^{20}$ −46.4 (*c*, 0.7 CH_2Cl_2); δ_H (200 MHz, $CDCl_3$) 1.35 (3H, s, Me_A*Me*$_B$C), 1.37 (3H, s, *Me*$_A$Me$_B$C), 2.40 (3H, s, *Me*$C_6H_4SO_2$), 3.89 (1H, dd, ^3J 4.0 and 1.5, C*H*[O]CHS), 4.09 (1H, dd, ^3J 9.0 and 6.0, $CHCH_AH_B$CMe$_2$), 4.23 (1H, dd, ^3J 9.0 and 7.0, $CHCH_AH_B$-CMe$_2$), 4.32 (1H, ddd, ^3J 7.0, 6.0 and 4.0, C*H*CH_AH_BCMe$_2$), 4.55 (1H, d, ^3J 1.5, CH[O]C*H*S), 7.23–7.28 (2H, m, Ar), 7.53–7.77 (3H, m, Ar), 7.83–7.97 (4H, m, Ar). IR and MS data were indistinguishable from **9a**.

(*S*)-*S*-[(4*R*),2α(*R**),3β(*S**)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)oxiran-2-yl]-*N*-[(4-methylphenyl)sulfonyl]-*S*-phenylsulfoximine 10a

Treatment of vinylsulfoximine **5** (0.84 g, 2 mmol) with lithium triphenylmethyl peroxide gave the *anti*-oxirane **10a** (0.655 g, 1.50 mmol, 76%) as a colourless oil, $[\alpha]_D^{20}$ −6.8 (*c*, 0.75 CH_2Cl_2); δ_H (200 MHz, $CDCl_3$) 1.36 (3H, s, Me_A*Me*$_B$C), 1.45 (3H, s, *Me*$_A$Me$_B$C), 2.39 (3H, s, *Me*$C_6H_4SO_2$), 3.95 (1H, dd, ^3J 2.5 and 1.5, C*H*[O]CHS), 4.06 (1H, dd, ^3J 8.5 and 7.0, $CHCH_AH_B$-CMe$_2$), 4.15 (1H, dd, ^3J 8.5 and 6.5, $CHCH_AH_B$CMe$_2$), 4.47 (1H, ddd, ^3J 7.0, 6.5 and 2.5, C*H*CH_AH_BCMe$_2$), 4.55 (1H, d, ^3J 1.5, CH[O]C*H*S), 7.24–7.28 (2H, m, Ar), 7.56–7.75 (3H, m, Ar), 7.85–8.01 (4H, m, Ar). IR and MS data were indistinguishable from **9a**. The *syn*-oxirane **10b**, which was obtained by column chromatography from the reaction using lithium *tert*-butyl peroxide as the oxidant, was a colourless oil: $[\alpha]_D^{20}$ −58.7 (*c*, 0.8 CH_2Cl_2); δ_H (200 MHz, $CDCl_3$) 1.27 (3H, s, Me_A*Me*$_B$C), 1.30 (3H, s, *Me*$_A$Me$_B$C), 2.39 (3H, s, *Me*$C_6H_4SO_2$), 3.56 (1H, dd, ^3J 3.0 and 1.5, C*H*[O]CHS), 3.81 (1H, dd, ^3J 8.5 and 6.0, $CHCH_AH_B$CMe$_2$), 4.12 (1H, dd, ^3J 8.5 and 7.0, $CHCH_AH_B$CMe$_2$), 4.27 (1H, ddd, ^3J 7.0, 6.0 and 3.0, C*H*CH_AH_BCMe$_2$), 4.58 (1H, d, ^3J 1.5, CH[O]C*H*S), 7.25–7.28 (2H, m, Ar), 7.56–7.76 (3H, m, Ar), 7.81–7.99 (4H, m, Ar). IR and MS data were indistinguishable from **9a**.

(2*R*,3*R*)-2-Bromo-3,4-*O*-isopropylidenebutane-1,3,4-triol 11

The *anti*-oxirane **9a** (200 mg, 0.475 mmol) was treated with magnesium bromide–diethyl ether and tetra-*n*-butylammonium borohydride as described above at room temp. for 48 h. Normal work up and purification[12] gave the bromohydrin **11** (62 mg, 0.32 mmol, 68%) as a colourless oil, $[\alpha]_D^{20}$ −9.4 (*c*, 0.9 CH_2Cl_2), ν_{max}(film)/cm^{-1} 3434, 797, 619; δ_H (200 MHz, $CDCl_3$) 1.37 (3H, s, Me_A*Me*$_B$C), 1.49 (3H, s, *Me*$_A$Me$_B$C), 2.26 (1H, br s, O*H*), 3.92–4.02 (3H, m, C*H*$_2$C*H*CH[Br]), 4.07–4.18 (2H, m, CH[Br]C*H*$_2$OH), 4.42 (1H, dt, ^3J 7.5 and 4.5, C*H*[Br]CH_2OH); *m*/*z* (EI) 209 (M^+ − Me, 27), 171 (M^+ − CH_2CH_2OH, 20), 155 (M^+ − Me_2CO_2, 25) (Found: M^+ − Me, 208.9818. $C_6H_{10}O_3Br$ requires 208.9814). (*S*)-2,2-Dimethyl-4-(2-hydroxyethyl)-1,3-

dioxolane **12** (21 mg, 0.15 mmol, 31%) was also isolated as a colourless oil, ν_{max}(film)/cm^{-1} 3444; δ_H (200 MHz, $CDCl_3$) 1.37 (3H, s, Me_A*Me*$_B$C), 1.43 (3H, s, *Me*$_A$Me$_B$C), 2.30 (1H, br s, O*H*), 3.60 (2H, m, CHC*H*$_2$CMe$_2$), 3.81 (2H, t, ^3J 6.0, C*H*$_2$OH), 4.10 (2H, dd, ^3J 8.0 and 6.0, C*H*$_2$CH$_2$OH), 4.30 (1H, m, CH$_2$C*H*CH$_2$); *m*/*z* (EI) 131 ($M^+ - Me$, 85), 101 ($M^+ - CH_2$-CH_2OH, 20), 71 ($M^+ - Me_2CO_2$, 80) (Found: $M^+ - Me$, 131.0675. $C_6H_{11}O_3$ requires 131.0642).

(2*R*,3*S*)-3,4-Epoxy-1,2-*O*-isopropylidenebutane-1,2-diol 13

To sodium hydride (65% in mineral oil; 8.5 mg, 0.226 mmol) in dry Et_2O (1 ml), (2*R*,3*R*)-2-bromo-3,4-*O*-isopropylidenebutane-1,3,4-triol **11** (50 mg, 0.226 mmol) in Et_2O (1 ml) was added and the mixture was stirred for 30 min. Phosphate buffer (pH 7; 3 ml) was added and the mixture was extracted with Et_2O (3 × 5 ml). The combined extracts were dried and concentrated under reduced pressure. Purification by column chromatography (5:1 petrol–ethyl acetate) gave the desired product (23 mg, 0.156 mmol, 69%) **13** as a colourless oil, $[a]_D^{20}$ +11.6 (*c*, 2.3 EtOH) {lit.[13] value $[a]_D^{20}$ +9.2 (*c*, 3.04 MeOH)}; δ_H (500 MHz, $CDCl_3$) 1.32 (3H, s, Me$_A$*Me*$_B$C), 1.41 (3H, s, *Me*$_A$Me$_B$C), 2.61 (1H, dd, ^3J 5.0 and 2.5, CH[O]CH$_A$*H*$_B$), 2.81 (1H, dd, ^3J 5.0 and 4.0, CH[O]C*H*$_A$H$_B$), 2.98 (1H, ddd, ^3J 6.5, 4.0 and 2.5, C*H*[O]CH$_A$H$_B$), 3.76 (1H, m, C*H*CH$_{A'}$H$_{B'}$CMe$_2$), 3.85 (1H, dd, ^3J 8.5 and 6.0, CHCH$_{A'}$*H*$_{B'}$CMe$_2$), 4.06 (1H, dd, ^3J 8.5 and 6.5, CHC*H*$_{A'}$H$_{B'}$CMe$_2$). Other spectroscopic data were identical to those reported.[13,15]

The two diastereoisomers (2*S*,3*R*) and (2*R*,3*R*) were prepared for comparison by the literature procedure of White *et al.*,[15] and the high field NMR data in which each proton can be clearly distinguished is listed below.

(2*R*,3*S*)-3,4-Epoxy-1,2-*O*-isopropylidenebutane-1,2-diol was prepared as a colourless oil, $[a]_D^{20}$ +11.45 (*c*, 2.2 EtOH); δ_H (500 MHz, $CDCl_3$) 1.32 (3H, s, Me$_A$*Me*$_B$C), 1.41 (3H, s, *Me*$_A$Me$_B$C), 2.60 (1H, dd, ^3J 5.0 and 2.5, CH[O]CH$_A$*H*$_B$), 2.80 (1H, dd, ^3J 5.0 and 4.0, CH[O]C*H*$_A$H$_B$), 2.91 (1H, ddd, ^3J 7.0, 4.0 and 2.5, C*H*[O]CH$_A$H$_B$), 3.81 (1H, dd, ^3J 8.5 and 6.5, CHCH$_{A'}$*H*$_{B'}$-CMe$_2$), 3.87 (1H, m, C*H*CH$_{A'}$H$_{B'}$CMe$_2$), 4.02–4.11 (1H, dd, ^3J 8.5 and 6.5, CHC*H*$_{A'}$H$_{B'}$CMe$_2$).

(2*R*,3*R*)-3,4-Epoxy-1,2-*O*-isopropylidenebutane-1,2-diol was prepared as a colourless oil, $[a]_D^{20}$ +1.2 (*c*, 2.4 EtOH); δ_H (500 MHz, $CDCl_3$) 1.35 (3H, s, Me$_A$*Me*$_B$C), 1.41 (3H, s, *Me*$_A$Me$_B$C), 2.65 (1H, dd, ^3J 5.0 and 2.5, CH[O]CH$_A$*H*$_B$), 2.79 (1H, dd, ^3J 5.0 and 4.0, CH[O]C*H*$_A$H$_B$), 3.02 (1H, ddd, ^3J 6.5, 4.0 and 2.5, C*H*[O]CH$_A$H$_B$), 3.84 (1H, dd, ^3J 8.5 and 5.5, CHCH$_{A'}$*H*$_{B'}$-CMe$_2$), 3.96 (1H, m, C*H*CH$_{A'}$H$_{B'}$CMe$_2$), 4.08 (1H, dd, ^3J 8.5 and 6.5, CHC*H*$_{A'}$H$_{B'}$CMe$_2$).

(1*R*)-1-[2α(*R**),3β(*S**)-3-(Phenylsulfonyl)oxiran-2-yl]ethane-1,2-diol 14

Toluene-*p*-sulfonic acid (30 mg, 0.176 mmol) was added to a solution of the *anti*-oxirane **8a** (0.5 g, 1.76 mmol) in dry THF (10 ml) and dry MeOH (10 ml). The reaction mixture was stirred for 16 h at room temp. Solid $NaHCO_3$ (*ca*. 0.2 g) was added, the suspension was washed with MeOH (10 ml) and concentrated under reduced pressure. Purification by column chromatography (1:1 petrol–ethyl acetate to pure ethyl acetate gradient) gave the corresponding diol **14** (0.341 g, 1.41 mmol, 80%) as a colourless solid, mp 143–144 °C, $[a]_D^{20}$ +62.4 (*c*, 1.0 MeOH) (Found: C, 48.9; H, 4.8. $C_{10}H_{12}O_5S$ requires C, 49.2; H, 5.0%); ν_{max}(KBr disc)/cm^{-1} 3494, 3380, 1584, 1086; δ_H (200 MHz, CD_3OD) 3.59 (2H, m, C*H*$_2$OH), 3.67 (1H, dd, ^3J 3.5 and 1.5, C*H*[O]CHSO$_2$Ph), 3.74 (1H, m, C*H*[OH]CH$_2$OH), 4.39 (1H, d, ^3J 1.5, CH[O]C*H*SO$_2$Ph), 7.62–7.78 (3H, m, Ph), 7.91–7.95 (2H, m, Ph); *m*/*z* (EI) 243 (MH^+, 10), 196 (28), 142 (70) and 78 (100).

(2*R*)-*trans*-3-(Phenylsulfonyl)oxiranecarbaldehyde 16

Diol **14** (300 mg, 1.24 mmol) in MeOH (4 ml) was added to a solution of sodium metaperiodate (0.531 g, 2.48 mmol) in H_2O (2 ml), and the suspension was stirred for 5 min. The reaction was diluted with H_2O (5 ml), resulting in a colourless solution. The product was extracted with CH_2Cl_2 (3 × 10 ml), dried and concentrated under reduced pressure to the crude product. Purification by column chromatography (1:1 petrol–ethyl acetate) gave the desired aldehyde **16** (260 mg, 1.23 mmol, 99%) as a colourless solid, mp 75–76 °C, $[a]_D^{20}$ +74.7 (*c*, 0.9 CH_2Cl_2); ν_{max}(film)/cm^{-1} 1734, 1586, 1086; δ_H (200 MHz, $CDCl_3$) 4.06 (1H, dd, ^3J 5.5 and 1.5, C*H*[O]CHSO$_2$Ph), 4.42 (1H, d, ^3J 1.5, CH[O]C*H*SO$_2$Ph), 7.57–7.81 (3H, m, Ph), 7.91–7.99 (2H, m, Ph), 9.14 (1H, d, ^3J 5.5, C*H*O); *m*/*z* (EI) 213 (MH^+, 7), 212 (M^+, 8) (Found: M^+, 212.0138. $C_9H_8O_4S$ requires 212.0132).

(2*R*)-*trans*-3-(Phenylsulfonyl)oxirane-2-methanol 17

Sodium borohydride (42 mg, 1.13 mmol) was added to a solution of the aldehyde **16** (200 mg, 0.943 mmol) in MeOH (4 ml) at −25 °C, and stirred for 90 min. Phosphate buffer (pH 7, 3 ml) was added and the product was extracted with CH_2Cl_2 (3 × 10 ml). The combined extracts were dried and concentrated under reduced pressure. Purification by column chromatography (1:1 petrol–ethyl acetate) gave the alcohol **17** (114 mg, 0.66 mmol, 70%) as a colourless solid, mp 73–74 °C, $[a]_D^{20}$ +94.0 (*c*, 1.0 CH_2Cl_2) (Found: C, 50.7; H, 4.9. $C_9H_{10}O_4S$ requires C, 50.5; H, 4.7%); ν_{max}(KBr disc)/cm^{-1} 3511, 1583, 1086; δ_H (200 MHz, $CDCl_3$) 3.85 (2H, m, C*H*$_2$OH), 4.05 (1H, m, C*H*[O]CHSO$_2$Ph), 4.26 (1H, d, ^3J 1.6, CH[O]C*H*SO$_2$Ph), 7.57–7.78 (3H, m, Ph), 7.93–7.98 (2H, m, Ph).

(2*R*)-*trans*-*tert*-Butyl(dimethyl){[3-(phenylsulfonyl)oxiran-2-yl]-methoxy}silane 15

tert-Butyldimethylsilyl chloride (79 mg, 0.526 mmol) and imidazole (36 mg, 0.526 mmol) were added to a solution of the alcohol **17** (100 mg, 0.439 mmol) in DMF (1 ml), and the mixture was stirred at room temp. for 40 h. The reaction mixture was diluted with petrol (10 ml) and washed with saturated aqueous sodium hydrogen carbonate (3 ml), brine (3 ml) and water (5 × 25 ml). The petrol extract was dried and concentrated under reduced pressure to give the silyl ether **15** (111 mg, 0.355 mmol, 81%) as a colourless oil, $[a]_D^{20}$ +49.0 (*c*, 1.8 CH_2Cl_2). Spectroscopic data were identical to those reported.[18]

Determination of optical purity of (2*R*)-*trans*-3-(phenylsulfonyl)oxirane-2-methanol 17; preparation of 3-(*R*)- and (*S*)-camphanoates of *trans*-3-hydroxymethyl-2-phenylsulfonyloxirane. General procedure

(*R*)- or (*S*)-Camphanic acid chloride (1.3 equiv.) and *N*,*N*-dimethylaminopyridine (1.3 equiv.) were added to a solution of the alcohol **17** in dry CH_2Cl_2 (1 ml per 0.1 mmol). The reaction mixture was stirred at room temp. for 16 h. After 16 h, the reaction mixture was concentrated under reduced pressure and the residue was treated with diethyl ether (1 ml per 0.1 mmol) and aqueous HCl (1.0 M; 2 ml per 0.1 mmol). The mixture was vigorously stirred for 10 min. The layers were separated and the ethereal layer was washed with saturated aqueous sodium carbonate (3 × 3 ml per 0.1 mmol). The etheral layer was dried, filtered through a small pad of silica and concentrated under reduced pressure to give the camphanoate ester as a colourless oil.

Camphanoate 18a

This compound was prepared from (*R*)-camphanic acid chloride and alcohol **15** according to the above procedure; δ_H (200 MHz, $CDCl_3$) 0.96 (3H, s, *Me*CC[Me$_A$Me$_B$]), 1.04 (3H, s, Me$_A$*Me*$_B$C), 1.12 (3H, s, *Me*$_A$Me$_B$C), 1.59–1.75 (1H, m), 1.85–2.09 (2H, m), 2.33–2.47 (1H, m), 3.93–3.97 (1H, m, C*H*[O]-CHSO$_2$Ph), 4.17 (1H, d, ^3J 1.5, CH[O]C*H*SO$_2$Ph), 4.26 (1H, dd,

^3J 13.0 and 4.5), 4.70 (1H, dd, ^3J 13.0 and 3.0), 7.58–7.78 (3H, m, Ph), 7.92–7.97 (2H, m, Ph).

Camphanoate 18b

This compound was prepared from (*S*)-camphanic acid chloride and alcohol **15** according to the above procedure; δ_H (200 MHz, $CDCl_3$) 0.90 (3H, s, *Me*CC[Me_AMe_B]), 1.05 (3H, s, Me_A*Me*$_B$C), 1.11 (3H, s, *Me*$_A$$Me_B$C), 1.61–1.76 (1H, m), 1.86–2.10 (2H, m), 2.35–2.49 (1H, m), 3.93–3.97 (1H, m, C*H*[O]-$CHSO_2Ph$), 4.17 (1H, d, ^3J 1.5, CH[O]C*H*SO_2Ph), 4.27 (1H, dd, ^3J 13.0 and 4.5), 4.71 (1H, dd, ^3J 13.0 and 3.0), 7.58–7.78 (3H, m, Ph), 7.92–7.96 (2H, m, Ph).

The key signals for comparison are at δ 0.90 and 0.96.

(4*R*)-2,2-Dimethyl-4-[2α(*R**),3β(*R**)-3-(phenylsulfonyl)-3-(phenylthio)oxiran-2-yl]-1,3-dioxolane

n-Butyllithium (2.0 M; solution in hexanes; 0.42 ml, 0.84 mmol) was added, dropwise, to a solution of the oxirane **8a** (200 mg, 0.704 mmol) in dry THF (6 ml) at −102 °C, and the mixture warmed to −95 °C and stirred at that temperature for 8 min. Phenyl benzenethiosulfonate[24] (264 mg, 1.06 mmol) in dry THF (4 ml) was added, dropwise. The reaction mixture was allowed to warm to −80 °C and stirred for 5 min, before being quenched with aqueous NH_4Cl (10%; 6 ml) and the mixture was allowed to warm to room temp. The mixture was extracted with CH_2Cl_2 (3 × 20 ml) and the combined extracts were dried, and concentrated under reduced pressure. Purification by column chromatography (3 : 1 petrol–ethyl acetate) gave oxirane **19** (191 mg, 0.486 mmol, 69%) as a colourless solid, mp 56–57 °C; $[\alpha]_D^{20}$ +26.9 (*c*, 0.9 CH_2Cl_2); ν_{max}(film)/cm^{-1} 1584, 1088; δ_H (200 MHz, $CDCl_3$) 1.35 (3H, s, Me_A*Me*$_B$C), 1.49 (3H, s, *Me*$_A$$Me_B$C), 4.04 (1H, d, ^3J 7.0, C*H*CH[O]CH_2), 4.13 (1H, m, CHC*H*[O]CH_2), 4.35 (2H, m, CHCH[O]C*H*$_2$), 7.11–7.63 (8H, m, Ar), 7.77–7.82 (2H, m, Ar); *m*/*z* (EI) 377 (M^+ − Me, 20), 317 (5), 282 (10).

(2*S*)-*S*-Phenyl 2-bromo-2-[(4*R**)-2,2-dimethyl-1,3-dioxolan-4-yl]ethanethioate 20

The oxirane **19** (60 mg, 0.153 mmol) in dry CH_2Cl_2 (1 ml) was added to a solution of magnesium bromide–diethyl ether (47 mg, 184 mmol) in dry diethyl ether (2 ml) at room temp., and stirred for 16 h. Phosphate buffer (pH 7; 3 ml) was added and the mixture was extracted with Et_2O (3 × 5 ml). The combined extracts were dried and concentrated under reduced pressure. Purification by column chromatography (5 : 1 petrol–ethyl acetate) gave the α-bromo thioester **20** (44 mg, 0.135 mmol, 88%) as a colourless solid, mp 60–61 °C; ν_{max}(film)/cm^{-1} 1692, 1478, 747; δ_H (200 MHz, $CDCl_3$) 1.38 (3H, s, Me_A*Me*$_B$C), 1.49 (3H, s, *Me*$_A$$Me_B$C), 3.98 (1H, dd, ^3J 9.0 and 5.0, CH_AH_BCHCH[Br]), 4.15 (1H, dd, ^3J 9.0 and 6.0, C*H*$_A$$H_B$CHCH[Br]), 4.49–4.63 (2H, m, CH_AH_BC*H*C*H*[Br]), 7.44 (5H, s, Ph); *m*/*z* (EI) 331 (MH^+, 5), 315 (M^+ − CH_3, 6), 257 (M^+ − Me_2C, CH_2OH, 20) (Found: M^+ − CH_3, 314.9687. $C_{12}H_{12}O_3SBr$ requires 314.9683).

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